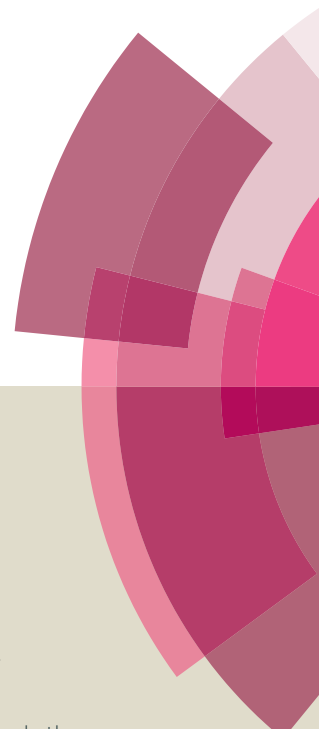
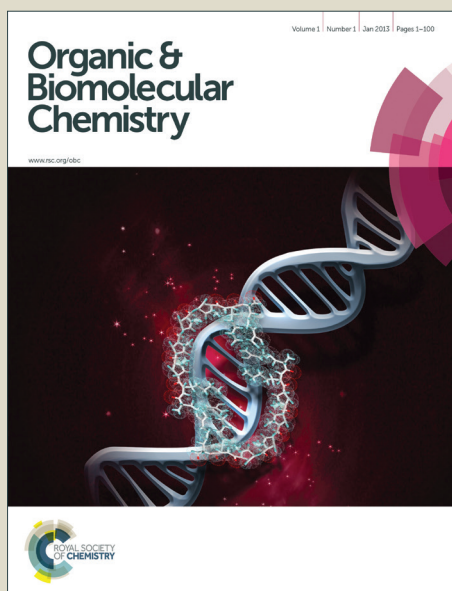


Organic & Biomolecular Chemistry

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: K. Watanabe, T. Mino, C. Hatta, S. Ito and M. Sakamoto, *Org. Biomol. Chem.*, 2015, DOI: 10.1039/C5OB01959A.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Journal Name

ARTICLE

Hydrazone-palladium catalyzed annulation of 1-allyl-2-bromobenzene derivatives with internal alkynes

Kohei Watanabe,^a Takashi Mino,^{a,b,*} Chikako Hatta,^a Shisei Ito^a and Masami Sakamoto^{a,b}Received 00th January 20xx,
Accepted 00th January 20xx

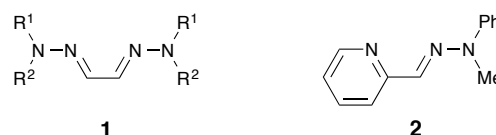
DOI: 10.1039/x0xx00000x

Annulation of 1-allyl-2-bromobenzene derivatives with internal alkynes using a hydrazone-palladium catalyst system proceeded smoothly and gave the corresponding polysubstituted naphthalene derivatives in good to high yields.

www.rsc.org/obc

Introduction

Polysubstituted naphthalene derivatives have become interestingly important because of their potential utility as π -conjugated functional materials, such as organic semiconductors and luminescent materials.¹ Furthermore, they are also basic skeletons of many biologically active compounds and pharmaceuticals such as an inhibitor of glycogen synthase kinase-3 (GSK-3).² Therefore, the synthetic methodologies for such structures have attracted significant attention and been developed.³ Among modern potential strategies to prepare polysubstituted naphthalene derivatives are the metal catalyzed coupling of aromatic compound with two internal alkynes.⁴ In 2014, Pham and co-workers reported Rh-catalyzed annulation of directing group-free monocyclic arenes with two internal alkynes *via* C-H activation for synthesis of polysubstituted naphthalenes.^{4p} However, the products of these methods are very restricted in terms of substituents of product because they are derived from two internal alkynes. On the other hand, there are some examples of the intramolecular annulation without internal alkyne for polysubstituted naphthalene derivatives, but these protocol required installing substituent in design of starting materials for selective synthesis.⁵ In 2002, Larock and co-workers reported that polysubstituted naphthalene can be prepared by annulation of *o*-alkenylaryl halides with internal alkynes using a triphenylphosphine-palladium catalyst system.⁶ This protocol *via* intramolecular Heck reaction is very effective for a selective approach to trisubstituted naphthalenes with the object of installing various substituents. However, this protocol is strongly limited in terms of substrates. For instance, the



- 1a:** R¹ = Ph, R² = Me
1b: R¹ = 2-Pyridyl, R² = Me
1c: R¹, R² = -(CH₂)₄-
1d: R¹, R² = -(CH₂)₅-
1e: R¹, R² = -(CH₂)₆-

Figure 1 Hydrazones **1** and **2**.

main starting materials of annulation are aryl iodides, which are reactive but expensive. Furthermore, all starting materials aside from one have electron-deficient olefin. When 1-allyl-2-iodobenzene, whose olefin has no substituent, reacted with diphenylacetylene, the corresponding naphthalene product was obtained in only 32% yield.^{6b} On the other hand, Chen and co-workers reported similar reaction which was achieved by C-H bond activation.⁷ However, this protocol was also tolerated only electron-deficient olefin bearing a phenyl group and required Cu(OAc)₂ as a co-catalyst in the presence of excess amount of TFA.

We recently demonstrated phosphine free hydrazone compounds (Figure 1) as an effective ligands for palladium-catalyzed C-C bond formations such as the Mizoroki-Heck,⁸ Suzuki-Miyaura,⁹ Sonogashira¹⁰ and Hiyama¹⁰ cross-coupling reactions of aryl halides. Herein, we report how limitation of substrates on palladium-catalyzed annulation of aryl bromides with internal alkynes for synthesis of polysubstituted naphthalene derivatives would be solved by using hydrazone as a ligand.

Results and discussion

Initially, we sought the optimal reaction conditions for a palladium-catalyzed synthesis of polysubstituted naphthalenes using hydrazone ligands. The reaction using 1-allyl-2-

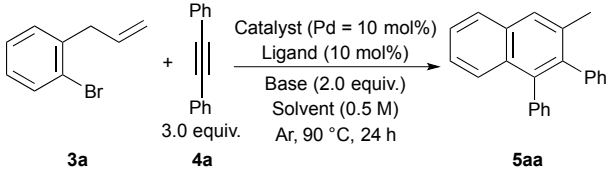
^a Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan
E-mail: tmno@faculty.chiba-u.jp

^b Molecular Chirality Research Center, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

[†] Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

bromobenzene and diphenylacetylene as model substrates was performed under an argon atmosphere at 90 °C for 24 h (Table 1). Using Pd(OAc)₂ and bishydrazone **1a** as a ligand, we observed that the reaction in the presence of Cs₂CO₃ in DMF as a solvent gave corresponding product **5aa** in 41% yield (Table 1, entry 1). Several palladium sources were tested (Table 1, entries 2-8). When we used Pd(TFA)₂, product **5aa** was obtained in 67% yield (Table 1, entry 6). On the other hand, palladium(0) sources, such as Pd₂(dba)₃ and Pd(PPh₃)₄ were not effective for this reaction (Table 1, entries 7 and 8). Next, we tested hydrazone ligands **1a-e** and **2** (Table 1, entries 6 and 9-14). While phenyl-methyl-type bishydrazone ligand **1a** afforded the corresponding product in high yield (Table 1, entry 6), 2-pyridyl-methyl-type bishydrazone ligand **1b** afforded slightly lower yield of product (Table 1, entry 9).

Table 1 Optimization of palladium-catalyzed annulation of 1-allyl-2-bromobenzene (**3a**) with diphenylacetylene (**4a**) using hydrazone ligand.^a

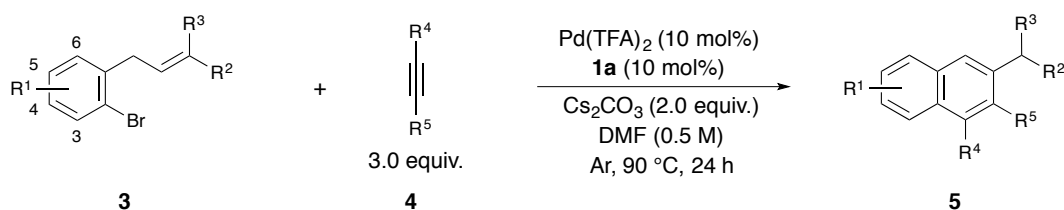


Entry	Catalyst	Ligand	Base	Solvent	Yield of 5aa [%]
1	Pd(OAc) ₂	1a	Cs ₂ CO ₃	DMF	41
2	PdCl ₂	1a	Cs ₂ CO ₃	DMF	57
3	[Pd(η -allyl)] ₂	1a	Cs ₂ CO ₃	DMF	14
4	Pd(acac) ₂	1a	Cs ₂ CO ₃	DMF	55
5	PdCl ₂ (MeCN) ₂	1a	Cs ₂ CO ₃	DMF	47
6	Pd(TFA) ₂	1a	Cs ₂ CO ₃	DMF	67
7	Pd ₂ (dba) ₃	1a	Cs ₂ CO ₃	DMF	8
8	Pd(PPh) ₄	-	Cs ₂ CO ₃	DMF	24
9	Pd(TFA) ₂	1b	Cs ₂ CO ₃	DMF	50
10	Pd(TFA) ₂	1c	Cs ₂ CO ₃	DMF	42
11	Pd(TFA) ₂	1d	Cs ₂ CO ₃	DMF	58
12	Pd(TFA) ₂	1e	Cs ₂ CO ₃	DMF	29
13	Pd(TFA) ₂	2	Cs ₂ CO ₃	DMF	45
14	Pd(TFA) ₂	PPh ₃ ^b	Cs ₂ CO ₃	DMF	17
15	Pd(TFA) ₂	1a	K ₂ CO ₃	DMF	15
16	Pd(TFA) ₂	1a	K ₃ PO ₄	DMF	25
17	Pd(TFA) ₂	1a	Ca(OH) ₂	DMF	Trace
18	Pd(TFA) ₂	1a	NaOAc	DMF	Trace
19	Pd(TFA) ₂	1a	Et ₃ N	DMF	Trace
20	Pd(TFA) ₂	1a	Cs ₂ CO ₃	DMA	28
21	Pd(TFA) ₂	1a	Cs ₂ CO ₃	NMP	42
22	Pd(TFA) ₂	1a	Cs ₂ CO ₃	DMSO	29
23	Pd(TFA) ₂	1a	Cs ₂ CO ₃	1,4-Dioxane	41
24	Pd(TFA) ₂	1a	Cs ₂ CO ₃	PhMe	39

^a Reaction conditions: **3a**, **4a** (3.0 equiv.), catalyst (Pd = 10 mol%), ligand (10 mol%), base (2.0 equiv.), solvent (0.5 M) at 90 °C for 24 h under Ar. ^b 20 mol% of PPh₃ was added.

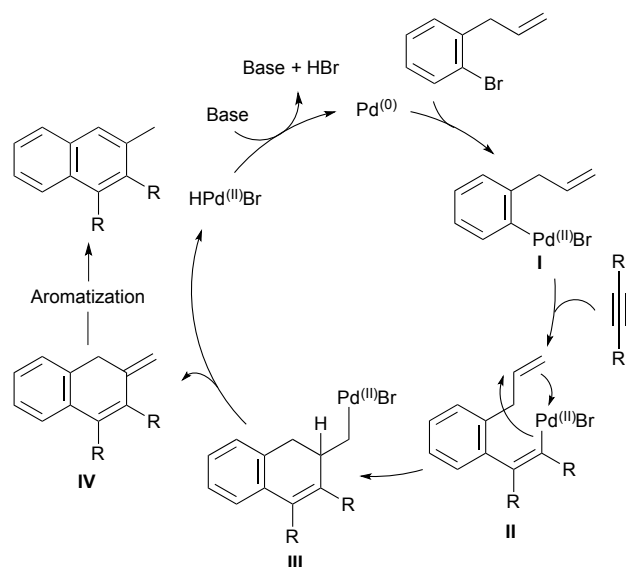
Using hydrazone ligands **1c-e** bearing 5-7 member rings gave the corresponding product in 42%, 58% and 29% yields, respectively (Table 1, entries 10-12). In the case of using pyridine-type monohydrazone ligand **2**, the desired product was obtained in 45% yield (Table 1, entry 13). On the other hand, the reaction proceeded inefficiently using triphenylphosphine as a ligand and gave the desired product in a low yield (Table 1, entry 14). As a result, we found phenyl-methyl-type bishydrazone ligand **1a** was the most suitable for this annulation (Table 1, entry 6). Next, the effects of various bases were investigated (Table 1, entries 6 and 15-19). Using Cs₂CO₃ led to the highest yield in this reaction (Table 1, entry 6). Various solvents were also tested (Table 1, entries 6 and 20-24). DMF was the most suitable solvent for this reaction (Table 1, entry 6).

With the optimized reaction conditions in hand (Table 1, Entry 6), we reacted 1-allyl-2-bromobenzene derivatives **3** with internal alkynes **4** at 80-110 °C to investigate the scope and limitation of this annulation (Table 2). The reactions of 1-allyl-2-bromobenzenes with an electron-donating or withdrawing group at the 5-position of the aromatic ring and diphenylacetylene **4a** proceeded and gave corresponding products in good to high yields respectively (Table 2, entries 2-5). Furthermore, 4-methyl-substituted aryl bromide **3f** was also tolerated (Table 2, entry 6). Aryl bromide **3g** bearing two methoxy groups on the aromatic ring reacted with **4a** at 110 °C to afford the desired product **5ga** in good yield (Table 2, entry 7). Moreover, we also succeeded in synthesizing polysubstituted phenanthrene derivative **5ha** in 66% yield (Table 2, entry 8). The reaction of bromide **3i**, whose olefin has a phenyl group, gave the corresponding product **5ia** in high yield (Table 2, entry 9). On the other hand, the annulation of **3j**, which has a prenyl group, did not afford the desired product (Table 2, entry 10). Presumably, this result indicated that bulky olefin bearing no electron-withdrawing group did not undergo an intramolecular Heck reaction because of steric and electronic effects. Next, we tested the reaction of 1-allyl-2-bromobenzene (**3a**) with various symmetrical internal alkynes **4**. When we employed diaryl acetylenes bearing electron-donating or withdrawing substituents on the aryl ring, the corresponding products were also obtained in good yields (Table 2, entries 11-14). However, the product was not observed in the case of using di-*p*-cyanophenyl acetylene (**4f**). This result indicated that internal alkyne bearing strong electron-withdrawing groups does not have enough coordination force to palladium complex because of the lack of electron density on the triple bond of the internal alkyne (Table 2, entry 15). Aliphatic internal alkyne such as 4-octyne (**4g**) was tolerated and afforded the desired product **5ag** in 65% yield. Unfortunately, the desired product was not obtained from the reaction of 1-allyl-2-bromobenzene (**3a**) with diethyl acetylenedicarboxylate (**4h**) because of the same reason in the case of **4f** (Table 2, entry 17). On the other hand, the use of an acetyl-protected 2-butyne-1,4-diol resulted in obtaining a naphthalene product **5ai** in 56% yield (Table 2, entry 18). In the case of using unsymmetric internal alkyne **4j**, the reaction gave

Table 2 Scope and limitation of annulation of aryl bromide **3** with internal alkynes **4** using hydrazone ligand.^aView Article Online
DOI: 10.1039/C5OB01959A

Entry	R ¹	R ²	R ³	R ⁴	R ⁵	Yield of 5 (%)
1	H	H	H (3a)	Ph	Ph (4a)	67 (5aa)
2	5-MeO	H	H (3b)	Ph	Ph (4a)	57 (5ba)
3 ^b	5-Me	H	H (3c)	Ph	Ph (4a)	60 (5ca)
4	5-Cl	H	H (3d)	Ph	Ph (4a)	47 (5da)
5 ^c	5-F	H	H (3e)	Ph	Ph (4a)	50 (5ea)
6 ^d	4-Me	H	H (3f)	Ph	Ph (4a)	58 (5fa)
7 ^d	4,5-diMeO	H	H (3g)	Ph	Ph (4a)	71 (5ga)
8	-(CH=CH) ₂ - (3,4)	H	H (3h)	Ph	Ph (4a)	66 (5ha)
9	H	Ph	H (3i)	Ph	Ph (4a)	81 (5ia)
10	5-MeO	Me	Me (3j)	Ph	Ph (4a)	N.D. ^e (5ja)
11 ^b	H	H	H (3a)	<i>p</i> -MeOC ₆ H ₄	<i>p</i> -MeOC ₆ H ₄ (4b)	60 (5ab)
12	H	H	H (3a)	<i>p</i> -MeC ₆ H ₄	<i>p</i> -MeC ₆ H ₄ (4c)	50 (5ac)
13 ^b	H	H	H (3a)	<i>p</i> -ClC ₆ H ₄	<i>p</i> -ClC ₆ H ₄ (4d)	64 (5ad)
14 ^b	H	H	H (3a)	<i>p</i> -FC ₆ H ₄	<i>p</i> -FC ₆ H ₄ (4e)	65 (5ae)
15	H	H	H (3a)	<i>p</i> -NCC ₆ H ₄	<i>p</i> -NCC ₆ H ₄ (4f)	N.D. ^e (5af)
16 ^b	H	H	H (3a)	<i>n</i> -Pr	<i>n</i> -Pr (4g)	65 (5ag)
17	H	H	H (3a)	COOEt	COOEt (4h)	N.D. ^e (5ah)
18 ^b	H	H	H (3a)	CH ₂ OAc	CH ₂ OAc (4i)	56 (5ai)
19 ^d	H	H	H (3a)	Me	Ph (4j)	62 ^f (5aj + 5aj')

^a Reaction conditions: Aryl bromide **3**, internal alkyne **4** (3.0 equiv.), Pd(TFA)₂ (10 mol%), **1a** (10 mol%), Cs₂CO₃ (2.0 equiv.), DMF (0.5 M) at 90 °C for 24 h under Ar. ^b This reaction was carried out at 100 °C. ^c This reaction was carried out at 80 °C. ^d This reaction was carried out at 110 °C. ^e Not detected. ^f The ratio of **5aj**/**5aj'** was 9/1 by ¹H NMR analysis.

**Scheme 1** Plausible reaction mechanism

1,3-dimethyl-2-phenylnaphthalene (**5aj**) and 1,2-dimethyl-3-phenylnaphthalene (**5aj'**) (**5aj**/**5aj'** = 9/1) (Table 2, entry 19).

A plausible mechanism of annulation of 1-allyl-2-bromobenzene derivatives with internal alkynes is illustrated in Scheme 1. At first,

oxidative addition of aryl bromide occurs and hydrazone-palladium(0) species inserts into carbon-bromide bond of 1-allyl-2-bromobenzene to generate aryl-palladium(II) complex **I**. Next, a triple bond of internal alkynes coordinates to palladium complex **I** and inserts into a carbon-palladium bond of complex **I** to generate intermediate **II**. Subsequently, intramolecular Heck reaction of intermediate **II** forms alkyl palladium(II) species **III**. alkyl-palladium(II) species **III** undergoes β -hydride elimination to generate intermediate **IV** and hydride-palladium(II) species. Intermediate **IV** easily transforms to the aromatic product via aromatization. On the other hand, after the reductive elimination of HBr from hydride-palladium(II) species by base, hydrazone-palladium(0) species is regenerated and the catalytic cycle is completed. We thought these palladium complexes were stabilized by hydrazone ligand, and this reaction proceeded smoothly in spite of the use of aryl bromides without electron-deficient olefin.

Conclusions

In summary, we found that palladium-catalyzed annulation of 1-allyl-2-bromobenzene derivatives **3** with internal alkynes **4** using hydrazone **1a** as a ligand proceeded smoothly and gave the corresponding polysubstituted naphthalene derivatives **5** in good to high yields even though low reactive aryl bromides without electron-deficient olefin were employed as starting materials.

Experimental section

Representative procedure for hydrazone-Pd catalyzed annulation.

A mixture of aryl bromide **3** (0.25 mmol), internal alkyne **4** (0.75 mmol), Pd(TFA)₂ (8.31 mg, 0.025 mmol), hydrazone ligand **1a** (6.66 mg, 0.025 mmol), and Cs₂CO₃ (0.1630 g, 0.50 mmol) in DMF (0.5 mL) under an Ar atmosphere was stirred for 24 h at 80–110 °C. After the reaction, the reaction was quenched with distilled water. The solution was extracted with ethyl acetate, washed with brine, dried over anhydrous MgSO₄, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane, hexane/ethyl acetate (v/v = 100–10/1) or hexane/chloroform (v/v = 1/1)) to afford the product **5**.

3-Methyl-1,2-diphenylnaphthalene (**5aa**)^{6b} (Table 1, Entry 6)

Compound **5aa** was obtained according to the general procedure at 90 °C in 67% yield (0.0493 g, 0.17 mmol); White solid; m.p. 149–151 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.77 (s, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.31 (td, *J* = 6.6, 1.8 Hz, 1H), 7.23–7.08 (m, 8H), 7.03 (dt, *J* = 6.4, 3.6 Hz, 2H), 2.26 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 140.6, 139.8, 139.4, 139.1, 138.6, 134.4, 132.9, 131.3, 131.0, 130.1, 127.5, 127.4, 127.1, 126.8, 126.3, 126.1, 125.7, 125.2, 21.9; EI-MS *m/z* (rel intensity): 294 (M⁺, 100).

6-Methoxy-3-methyl-1,2-diphenylnaphthalene (**5ba**) (Table 2, Entry 2)

Compound **5ba** was obtained according to the general procedure at 90 °C in 57% yield (0.0459 g, 0.14 mmol); Yellow solid; m.p. 118–120 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.67 (s, 1H), 7.38 (d, *J* = 9.2 Hz, 1H), 7.22–6.96 (m, 12H), 3.93 (s, 3H), 2.23 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 157.5, 140.6, 139.5, 138.5, 137.7, 135.0, 134.1, 130.9, 130.3, 128.5, 127.44, 127.36, 126.7, 126.4, 126.3, 126.0, 117.7, 105.1, 55.3, 21.9; EI-MS *m/z* (rel intensity): 324 (M⁺, 100); HRMS (APPI): calcd for C₂₄H₂₀O [M]⁺ 324.1509, found 324.1499.

3,6-Dimethyl-1,2-diphenylnaphthalene (**5ca**) (Table 2, Entry 3)

Compound **5ca** was obtained according to the general procedure at 100 °C in 60% yield (0.0464 g, 0.15 mmol); Yellow solid; m.p. 122–124 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.67 (s, 1H), 7.60 (s, 1H), 7.36 (d, *J* = 8.7 Hz, 1H), 7.24–7.00 (m, 11H), 2.49 (s, 3H), 2.23 (d, *J* = 0.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 140.7, 139.5, 138.9, 138.3, 135.3, 134.4, 133.1, 131.0, 130.2, 129.5, 127.5, 127.4, 127.3, 126.8, 126.6, 126.2, 126.1, 126.0, 21.9, 21.5; EI-MS *m/z* (rel intensity): 308 (M⁺, 100); HRMS (APCI): calcd for C₂₄H₂₁ [M + H]⁺ 309.1638, found 309.1628.

6-Chloro-3-methyl-1,2-diphenylnaphthalene (**5da**) (Table 2, Entry 4)

Compound **5da** was obtained according to the general procedure at 90 °C in 47% yield (0.0385 g, 0.12 mmol); White solid; m.p. 137–138 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.80 (d, *J* = 2.1 Hz, 1H), 7.67 (s, 1H), 7.40 (d, *J* = 9.0 Hz, 1H), 7.24–6.99 (m, 11H), 2.24 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 140.14, 140.11, 138.9, 138.7, 135.9, 133.5, 131.5, 130.9, 130.0, 129.6, 128.6, 127.6, 127.5, 126.53, 126.50, 126.3, 126.0, 125.6, 21.9; EI-MS *m/z* (rel intensity): 328 (M⁺, 100); HRMS (APPI): calcd for C₂₃H₁₇Cl [M]⁺ 328.1013, found 328.1005.

6-Fluoro-3-methyl-1,2-diphenylnaphthalene (**5ea**) (Table 2, Entry 5)

Compound **5ea** was obtained according to the general procedure at 80 °C in 50% yield (0.0386 g, 0.12 mmol); White solid; m.p. 147–149 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.70 (s, 1H), 7.48–7.41 (m, 2H), 7.23–7.00 (m, 11H), 2.24 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 162.3, 159.0, 140.3, 139.2, 139.1, 138.7, 135.8, 133.7 (d, *J* = 9.3 Hz), 130.9, 130.1, 129.5 (d, *J* = 8.8 Hz), 128.4, 127.5 (d, *J* = 5.0 Hz), 126.7 (d, *J* = 5.3 Hz), 126.3 (d, *J* = 21.8 Hz), 115.3 (d, *J* = 24.9 Hz), 109.9 (d, *J* = 20.2 Hz), 21.9; EI-MS *m/z* (rel intensity): 312 (M⁺, 100); HRMS (APPI): calcd for C₂₃H₁₇F [M]⁺ 312.1309, found 312.1302.

3,7-Dimethyl-1,2-diphenylnaphthalene (**5fa**) (Table 2, Entry 6)

Compound **5fa** was obtained according to the general procedure at 110 °C in 58% yield (0.0447 g, 0.15 mmol); White solid; m.p. 134–135 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.74 (d, *J* = 8.5 Hz, 1H), 7.72 (s, 1H), 7.30 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.22–7.07 (m, 9H), 7.03–7.00 (m, 2H), 2.36 (s, 3H), 2.23 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 140.7, 139.9, 139.5, 137.9, 134.8, 133.3, 131.3, 131.1, 131.0, 130.1, 128.0, 127.43, 127.36, 127.1, 127.0, 126.2, 126.0, 125.6, 21.9, 21.8; EI-MS *m/z* (rel intensity): 308 (M⁺, 100); HRMS (APCI): calcd for C₂₄H₂₁ [M + H]⁺ 309.1638, found 309.1628.

3-Methyl-6,7-dimethoxy-1,2-diphenylnaphthalene (**5ga**) (Table 2, Entry 7)

Compound **5ga** was obtained according to the general procedure at 110 °C in 71% yield (0.0624 g, 0.18 mmol); Yellow solid; m.p. 203–205 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.63 (s, 1H), 7.23–7.08 (m, 9H), 7.04–7.01 (m, 2H), 6.76 (s, 1H), 4.02 (s, 3H), 3.69 (s, 3H), 2.22 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 149.3, 148.8, 140.8, 140.0, 138.1, 137.4, 132.6, 130.8, 130.2, 128.7, 127.5, 127.4, 126.6, 126.3, 126.0, 125.9, 105.61, 105.56, 55.9, 55.5, 21.7; EI-MS *m/z* (rel intensity): 354 (M⁺, 100); HRMS (APCI): calcd for C₂₅H₂₃O₂ [M + H]⁺ 355.1693, found 355.1681.

2-Methyl-3,4-diphenylphenanthrene (**5ha**) (Table 2, Entry 8)

Compound **5ha** was obtained according to the general procedure at 90 °C in 66% yield (0.0571 g, 0.17 mmol); Yellow solid; m.p. 137–140 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.81–7.69 (m, 4H), 7.38–7.33 (m, 2H), 7.20–6.94 (m, 11H), 2.23 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 143.1, 142.1, 141.0, 138.9, 134.9, 133.5, 132.8, 131.0, 130.7, 130.2, 129.0, 128.5, 128.2, 127.8, 127.7, 127.4, 127.1, 127.0, 126.3, 125.8, 125.4, 124.9, 21.6; EI-MS *m/z* (rel intensity): 344 (M⁺, 100); HRMS (APPI): calcd for C₂₇H₂₀ [M]⁺ 344.1560, found 344.1549.

3-Cinnamyl-1,2-diphenylnaphthalene (**5ia**) (Table 2, Entry 9)

Compound **5ia** was obtained according to the general procedure at 90 °C in 81% yield (0.0752 g, 0.20 mmol); Yellow solid; m.p. 153–155 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.68 (s, 1H), 7.48–7.42 (m, 2H), 7.35–7.30 (m, 1H), 7.22–7.07 (m, 11H), 6.97–6.89 (m, 4H), 3.93 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 140.8, 139.9, 139.7, 139.3, 139.1, 137.4, 132.7, 131.5, 130.9, 130.4, 129.1, 128.1, 127.9, 127.5, 127.4, 127.3 (2C), 126.8, 126.3, 126.1, 125.8, 125.6, 40.5; EI-MS *m/z* (rel intensity): 370 (M⁺, 100); HRMS (APCI): calcd for C₂₉H₂₂ [M]⁺ 370.1716, found 370.1705.

1,2-Bis(4-methoxyphenyl)-3-methylnaphthalene (**5ab**)^{3a} (Table 2, Entry 11)

Compound **5ab** was obtained according to the general procedure at 100 °C in 69% yield (0.0603 g, 0.17 mmol); Cream solid; m.p. 201–202 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.74 (s, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.44 (td, *J* = 8.0, 1.1 Hz, 1H), 7.30 (ddd, *J* = 8.2, 7.6, 1.1 Hz, 1H), 7.02 (dt, *J* = 8.7, 2.0 Hz, 2H), 6.93 (dt, *J* = 8.7, 2.8 Hz, 2H), 6.75 (tt, *J* = 8.9, 2.8 Hz, 4H), 3.78 (s, 3H), 3.76 (s, 3H), 2.25 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 157.8, 157.6, 139.8, 138.5, 134.9, 133.1, 132.8, 132.0, 131.8, 131.7, 131.1,

127.2, 127.0, 126.8, 125.6, 125.1, 113.0, 112.9, 55.1, 55.0, 22.0; EI-MS m/z (rel intensity): 354 (M^+ , 100); HRMS (APCI): calcd for $C_{25}H_{22}O_2 [M]^+$ 354.1614, found 354.1614.

3-Methyl-1,2-di-*p*-tolynaphthalene (5ac)^{3a} (Table 2, Entry 12)
Compound **5ac** was obtained according to the general procedure at 90 °C in 50% yield (0.0404 g, 0.13 mmol); White solid; m.p. 159–160 °C; 1H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, J = 8.1 Hz, 1H), 7.74 (s, 1H), 7.44 (q, J = 7.0 Hz, 2H), 7.28 (t, J = 7.1 Hz, 1H), 7.03–6.90 (m, 8H), 2.30 (s, 3H), 2.27 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.8, 138.6, 137.6, 136.4, 135.6, 135.4, 134.7, 132.8, 131.5, 130.8, 129.9, 128.2, 128.1, 127.2, 127.0, 126.8, 125.5, 125.1, 22.0, 21.21, 21.18; EI-MS m/z (rel intensity): 322 (M^+ , 100); HRMS (ESI): calcd for $C_{25}H_{22}Na [M + Na]^+$ 345.1614, found 345.1610.

1,2-Bis(4-chlorophenyl)-3-methylnaphthalene (5ad) (Table 2, Entry 13)

Compound **5ad** was obtained according to the general procedure at 100 °C in 64% yield (0.0587 g, 0.16 mmol); White solid; m.p. 166 °C; 1H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, J = 8.2 Hz, 1H), 7.77 (s, 1H), 7.50–7.31 (m, 3H), 7.20 (t, J = 6.4 Hz, 4H), 7.01 (d, J = 4.6 Hz, 2H), 6.95 (d, J = 4.6 Hz, 2H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.7, 138.6, 137.5, 137.3, 134.1, 132.9, 132.5, 132.3, 132.2, 131.3, 131.0, 128.0, 127.93, 127.89, 127.2, 126.4, 126.1, 125.6, 21.8; EI-MS m/z (rel intensity): 362 (M^+ , 88); HRMS (APPI): calcd for $C_{23}H_{16}Cl_2 [M]^+$ 362.0624, found 362.0623.

1,2-Bis(4-fluorophenyl)-3-methylnaphthalene (5ae) (Table 2, Entry 14)

Compound **5ae** was obtained according to the general procedure at 100 °C in 65% yield (0.0537 g, 0.16 mmol); White solid; m.p. 210 °C; 1H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, J = 8.1 Hz, 1H), 7.77 (s, 1H), 7.50–7.42 (m, 2H), 7.33 (t, J = 7.9 Hz, 1H), 7.06–6.86 (m, 8H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.5 (d, J = 245.5 Hz), 161.3 (d, J = 245.2 Hz), 139.1, 137.8, 136.3 (d, J = 3.3 Hz), 135.1 (d, J = 3.3 Hz), 134.4, 133.0, 132.4 (d, J = 7.8 Hz), 131.5 (d, J = 7.8 Hz), 131.3, 127.7, 127.2, 126.5, 125.9, 125.5, 114.8 (d, J = 5.7 Hz), 114.5 (d, J = 5.8 Hz), 21.8; EI-MS m/z (rel intensity): 330 (M^+ , 100); HRMS (APPI): calcd for $C_{23}H_{16}F_2 [M]^+$ 330.1215, found 330.1211.

3-Methyl-1,2-dipropylnaphthalene (5ag)¹¹ (Table 2, Entry 16)

Compound **5ag** was obtained according to the general procedure at 100 °C in 65% yield (0.0366 g, 0.16 mmol); Colorless oil; 1H NMR (300 MHz, $CDCl_3$): δ 7.95 (d, J = 8.1 Hz, 1H), 7.67 (d, J = 9.3 Hz, 1H), 7.49 (s, 1H), 7.43–7.33 (m, 2H), 3.05–3.00 (m, 2H), 2.78–2.73 (m, 2H), 2.48 (s, 3H), 1.72–1.53 (m, 4H), 1.14–1.06 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.4, 135.7, 134.9, 132.4, 131.0, 127.7, 126.8, 124.8, 124.5, 123.9, 32.3, 30.9, 24.5, 23.8, 20.8, 14.9 (2C); EI-MS m/z (rel intensity): 226 (M^+ , 60).

3-Methyl-1,2-naphthalene dimethanol, 1,2-diacetate (5ai) (Table 2, Entry 18)

Compound **5ai** was obtained according to the general procedure at 100 °C in 56% yield (0.0399 g, 0.14 mmol); White solid; m.p. 50–51 °C; 1H NMR (300 MHz, $CDCl_3$): δ 8.09–8.05 (m, 1H), 7.79–7.72 (m, 2H), 7.54–7.47 (m, 2H), 5.72 (s, 2H), 5.46 (s, 2H), 2.57 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.9, 170.7, 135.2, 133.8, 132.9, 131.5, 131.2, 130.3, 127.8, 126.5, 126.3, 124.1, 60.8, 59.7, 20.93, 20.89, 20.3; EI-MS m/z (rel intensity): 286 (M^+ , 8); HRMS (APPI): calcd for $C_{17}H_{18}O_4Na [M + Na]^+$ 309.1097, found 309.1097.

1,3-Dimethyl-2-phenylnaphthalene (5aj)¹² (including **1,2-dimethyl-3-phenylnaphthalene (5aj')**¹³) (Table 2, Entry 19)

The mixture of **5aj** and **5aj'** was obtained according to the general procedure at 110 °C in 62% yield (0.0536 g, 0.16 mmol) (**5aj/5aj'** = 9/1); Colorless oil; 1H NMR (300 MHz, $CDCl_3$): δ 8.02 (m, 1H), 7.81–7.74 (m, 1H), 7.66 (**5aj'** (minor)) and 7.60 (**5aj** (major)) (s, 1H),

7.51–7.35 (m, 5H), 7.27–7.18 (m, 2H), 2.49 (**5aj'** (minor)) and 2.37 (**5aj** (major)) (s, 3H), 2.15 (**5aj** (major)) and 2.13 (**5aj'** (minor)) (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.6 (**5aj** (major)), 140.4 (**5aj'** (minor)), 140.2 (**5aj** (major)), 138.3 (**5aj'** (minor)), 135.4 (**5aj'** (minor)), 134.5 (**5aj** (major)), 133.1 (**5aj'** (minor)), 132.9 (**5aj** (major)), 131.9 (**5aj'** (minor)), 131.7 (**5aj'** (minor)), 131.4 (**5aj** (major)), 131.2 (**5aj** (major)), 130.2 (**5aj'** (minor)), 129.3 (**5aj** (major)), 128.3, 127.7 (**5aj** (major)), 127.1 (**5aj'** (minor)), 126.92 (**5aj'** (minor)), 126.86 (**5aj'** (minor)), 126.7 (**5aj** (major)), 126.3 (**5aj'** (minor)), 125.8 (**5aj** (major)), 125.5 (**5aj** (major)), 125.2 (**5aj** (major)), 124.83 (**5aj'** (minor)), 124.78 (**5aj'** (minor)), 124.4 (**5aj** (major)), 22.0 (**5aj** (major)), 21.2 (**5aj'** (minor)), 17.6 (**5aj'** (minor)), 16.5 (**5aj** (major)); EI-MS m/z (rel intensity): 232 (M^+ , 100).

Acknowledgements

This work was supported by the COE Program in Chiba University.

Notes and references

- (a) U. Mitschke and P. Bäuerle, *J. Mater. Chem.*, 2000, **10**, 1471; (b) M. D. Watson, A. Fechtenkötter and K. Müllen, *Chem. Rev.*, 2001, **101**, 1267; (c) M. Bendikov and F. Wudl, *Chem. Rev.*, 2004, **104**, 4891; (d) J. E. Anthony, *Angew. Chem. Int. Ed.*, 2008, **47**, 452; (e) I. Kaur, N. N. Stein, R. P. Kopreski and G. P. Miller, *J. Am. Chem. Soc.*, 2008, **131**, 3424; (f) J. E. Anthony, A. Facchetti, M. Heeney and S. R. Marder, *Adv. Mater.*, 2010, **22**, 3876.
- H. Zou, L. Zhou, Y. Li, Y. Cui, H. Zhong, Z. Pan, Z. Yanga and J. Quan, *J. Med. Chem.*, 2010, **53**, 994.
- (a) Z. Duan, K. Nakajima, T. Takahashi, *Chem. Commun.*, 2001, 1672; (b) C. B. Koning, A. L. Rousseau and W. A. L. Otterlo, *Tetrahedron*, 2003, **59**, 7; (c) S. S. Moleele, J. P. Michael and C. B. Koning, *Tetrahedron*, 2006, **62**, 2831; (d) A. C. Glass, B. B. Morris, L. N. Zakharov and S.-Y. Liu, *Org. Lett.*, 2008, **10**, 4855; (e) A. N. Lowell, M. W. Fennie and M. C. Kozlowski, *J. Org. Chem.*, 2007, **73**, 1911; (f) W. A. L. Otterlo and C. B. Koning, *Chem. Rev.*, 2009, **109**, 3743; (g) S.-G. Li, X.-Q. Hu, Z.-X. Jia and P.-F. Xu, *Tetrahedron*, 2010, **66**, 8557; (h) H. Xu, S. Li, H. Liu, H. Fu and Y. Jiang, *Chem. Commun.*, 2010, **46**, 7617; (i) K. Sakabe, H. Tsurugi, K. Hirano, T. Satoh and M. Miura, *Chem. Eur. J.*, 2010, **16**, 445; (j) D. Mal, A. K. Jana, P. Mitra and K. Ghosh, *J. Org. Chem.*, 2011, **76**, 3392; (k) C. C. Malakar, D. Schmidt, J. Conrad and U. Beifuss, *Org. Lett.*, 2011, **13**, 1972; (l) J.-G. Wang, M. Wang, J.-C. Xiang, Y.-P. Zhu, W.-J. Xue and A.-X. Wu, *Org. Lett.*, 2012, **14**, 6060; (m) A. C. Mantovani, D. F. Back and G. Zeni, *Eur. J. Org. Chem.*, 2012, 4574; (n) C. C. Malakar, K. Sudheendran, H.-G. Imrich, S. Mika and U. Beifuss, *Org. Biomol. Chem.*, 2012, **10**, 3899; (o) P. Qian, F. Chen and C. Pan, *Synth. Commun.*, 2012, **42**, 3242; (p) R. M. Patel and N. P. Argade, *Org. Lett.*, 2013, **15**, 14; (q) K. Sudheendran, C. C. Malakar, J. Conrad and U. Beifuss, *Adv. Synth. Catal.*, 2013, **355**, 2400; (r) S. Manojveer and R. Balamurugan, *Org. Lett.*, 2014, **16**, 1712; (s) Z. Lou, S. Zhang, C. Chen, X. Pang, M. Li and L. Wen, *Adv. Synth. Catal.*, 2014, **356**, 153.
- (a) M. A. Bennett and E. Wenger, *Organometallics*, 1995, **14**, 1267; (b) D. Peña, D. Pérez, E. Gutiérrez, L. Casted, *J. Am. Chem. Soc.*, 1999, **121**, 5827–5828; (c) T. Yasukawa, T. Satoh, M. Miura and M. Nomura, *J. Am. Chem. Soc.*, 2002, **124**, 12680; (d) S. Kawasaki, T. Satoh, M. Miura, M. Nomura, J.

- Org. Chem.*, 2003, **68**, 6836; (e) W. Huang, X. Zhou, K. Kanno and T. Takahashi, *Org. Lett.*, 2004, **6**, 2429; (f) K. Ueura, T. Satoh and M. J. Mura, *Org. Chem.*, 2007, **72**, 5362; (g) N. Umeda, H. Tsurugi, T. Satoh and M. Miura, *Angew. Chem. Int. Ed.*, 2008, **47**, 4019; (h) Y.-T. Wu, K.-H. Huang, C.-C. Shin and T.-C. Wu, *Chem. Eur. J.*, 2008, **14**, 6697; (i) J.-C. Hsieh, C.-H. Cheng, *Chem. Commun.*, 2008, 2992; (j) J. Wu, W. Cui, X. Mi, Y. Li and Y. Wu, *Chem. Commun.*, 2010, **46**, 6771; (k) T. Fukutani, K. Hirano, T. Satoh and M. Miura, *J. Org. Chem.*, 2011, **76**, 2867; (l) H. Zhang, X. Cui, X. Yao, J. Zhang and Y. Wu, *Org. Lett.* 2012, **14**, 3012; (m) L. Adak and N. Yoshikai, *Tetrahedron*, 2012, **68**, 5167; (n) F. Jafarpour, H. Hazrati and S. Nouraldinmoussa, *Org. Lett.*, 2013, **15**, 3816; (o) K. Komeyama, T. Kashiwara and K. Takaki, *Tetrahedron Lett.*, 2013, **54**, 5659; (p) M. V. Pham and N. Cramer, *Angew. Chem. Int. Ed.*, 2014, **53**, 3484.
- 5 (a) N. Asao, K. Sato, Menggenbateer and Y. Yamamoto, *J. Org. Chem.*, 2005, **70**, 3682; (b) J. Zhao, C. O. Hughes and F. D. Toste, *J. Am. Chem. Soc.*, 2006, **128**, 7436; (c) A. S. Dudnik, T. Schewier and V. Gevorgyan, *Org. Lett.*, 2008, **10**, 1465; (d) C. Zhan, Z. Lu, C. Fu, and S. Ma, *Chem. Eur. J.*, 2009, **15**, 11083; (e) Z.-Q. Wang, Y. Liang, Y. Sei, M.-B. Zhou and J.-H. Li, *Chem. Commun.*, 2009, 5242; (f) A. R. Jagdal, J. H. Park and S. W. Youn, *J. Org. Chem.*, 2011, **76**, 7204; (g) D. Kang, J. Kim, S. Oh, and P. H. Lee, *Org. Lett.*, 2012, **14**, 5636; (h) L. S. Kocsis, E. Benedetti and K. M. Brummond, *Org. Lett.*, 2012, **14**, 4430; (i) X. Zhang, X. Jia, N. Liu, X. Guo, Y. Song and X. Fan, *Tetrahedron*, 2013, **69**, 5374; (j) R. S. Reddy, P. K. Prasad, B. B. Ahuja and A. Sudalai, *J. Org. Chem.*, 2013, **78**, 5045; (k) Z. Chen, X. Jia, C. Ye, G. Qiu and J. Wu, *Chem. Asian. J.*, 2014, **9**, 126.
- 6 (a) Q. Huang and R. C. Larock, *Org. Lett.*, 2002, **4**, 2505; (b) Q. Huang and R. Q. Larock, *J. Org. Chem.*, 2003, **68**, 7342.
- 7 P. Gandeepan and C.-H. Cheng, *Org. Lett.*, 2011, **15**, 2084.
- 8 (a) T. Mino, Y. Shirae, Y. Sasai, M. Sakamoto and T. Fujita, *J. Org. Chem.*, 2006, **71**, 6834; (b) T. Mino, H. Sindo, T. Kaneda, T. Koizumi, Y. Kasashim and M. Sakamoto, *Tetrahedron Letters*, 2009, **50**, 5358; (c) T. Mino, M. Shibuya, S. Suzuki, K. Hirai, M. Sakamoto and T. Fujita, *Tetrahedron*, 2012, **68**, 429; (d) T. Mino, K. Watanabe, T. Abe, T. Kogure and M. Sakamoto, *Heterocycles*, 2013, **87**, 2015.
- 9 (a) T. Mino, Y. Shirae, M. Sakamoto and T. Fujita, *J. Org. Chem.*, 2005, **70**, 2191; (b) T. Mino, Y. Shirae, M. Sakamoto and T. Fujita, *Synlett*, 2003, 882; (c) T. Mino, E. Yoshizawa, K. Watanabe, T. Abe, K. Hirai and M. Sakamoto, *Tetrahedron Letters*, 2014, **55**, 3184.
- 10 (a) T. Mino, Y. Shirae, T. Saito, M. Sakamoto and T. Fujita, *J. Org. Chem.*, 2006, **71**, 9499; (b) T. Mino, S. Suzuki, K. Hirai, M. Sakamoto and T. Fujita, *Synlett*, 2011, 1277.
- 11 E. Yoshikawa, K. V. Radhakrishnan and Y. Yamamoto, *J. Am. Chem. Soc.*, 2000, **122**, 7280.
- 12 R. Dupont and P. Cotellet, *Synthesis*, 1999, **9**, 1651.
- 13 J.-J. Zhang, C.-S. Yan, Y. Peng, Z.-B. Luo, B.-X. Xu and Y.-W. Wang, *Org. Biomol. Chem.*, 2013, **11**, 2498.